

PATENT SPECIFICATION

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(19)



(54) PHOTOPOLYMERISABLE COMPOSITIONS FOR AQUEOUS PROCESSED PHOTORESISTS

(71) We, DYNACHEM CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of 2632 Michelle Drive, Tustin, California 92680, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a new and improved photopolymerizable composition and to a method for using the same. More particularly, the invention relates to a light-sensitive composition which can be readily developed by means of an aqueous alkaline solution to yield a product which is useful as a flexible photopolymerizable film. These compositions are particularly useful as photoresists in the manufacture of printed circuits because the resists formed therefrom are impervious to conventional plating and etching solutions. They are also useful for making screen stencils and printing plates.

The desirability of forming light-sensitive compositions which can be developed without the need for the conventional organic solvents has long been recognized. Organic solvents are costly, hazardous with respect to toxicity and flammability, and pollute the air and water. Systems which are developable in aqueous alkaline solutions are described in British Patent No. 1,361,298. While these compositions are most useful for their intended purpose, when used as dry film laminates they suffer the disadvantages of poor flexibility. A brittle film will not only crack during and prior to use, but it also fails to slit properly when the master rolls are cut to the specific size required by the user. The edges of the slit rolls sliver and the photopolymerizable layer separates from its polyester base. In areas where this occurs, the layer will not expose properly and, therefore, loses its ability to perform as a resist after development. As a result, a brittle film simply cannot be used in flexible circuit-building

applications, since it will crack and fall off the circuit board when it is bent.

In the prior art, external plasticizers have been incorporated in the photopolymerizable material to overcome the poor flexibility. This, however, has not been entirely satisfactory because such plasticizers tend to migrate within the film on ageing and contribute heavily to the cold flow. Cold flow cannot be tolerated because the film rolls are stored under a static load and, after a short time, the photopolymerizable material begins to ooze out from between the layers. Thereafter, the material which has oozed out fuses along the edge of the rolls and makes it difficult, if not impossible, to unroll the material evenly and without destroying the composite film. Furthermore, external plasticizers are volatile. During the manufacturing of the film, if drying is not precisely controlled, some of the plasticizer will volatilize, thereby returning the film to its brittle state.

It has now been found that aqueous developable photopolymerizable compositions can be produced which may be formed into dry films having excellent flexibility in the absence of external plasticizers and high resistance to cold flow. Upon exposure, the polymerized portions of these compositions have outstanding resistance to the typical solutions encountered in the fabrication of printed circuits and chemically machined parts, including alkaline etchants and alkaline plating solutions.

The present invention provides a photopolymerisable composition comprising:

(A) from 10 to 60 parts by weight of one or more addition polymerizable non-gaseous compounds having a boiling point above 100°C., and at least one terminal ethylenic group;

(B) from 1 to 10 parts by weight of a free-radical generating photoinitiator; and

(C) from 40 to 90 parts by weight of a preformed macromolecular binding agent which is a polymer of

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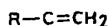
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- (i) from 40—60% by weight of a first monomeric material which comprises one or more styrene-type compounds of the general formula:



wherein R is hydrogen, an alkyl group having from 1 to 6 carbon atoms or a halogen atom and the benzene ring may be substituted by from 1 to 5 substituents which are nitro, alkoxy, acyl, carboxyl, sulpho or hydroxyl groups or halogen atoms;

- (ii) from 15—45% by weight of a second monomeric material which comprises one or more alkyl acrylates, alkyl methacrylates, hydroxyalkyl acrylates or hydroxyalkyl methacrylates wherein the alkyl groups have from 1 to 12 carbon atoms and the hydroxyalkyl groups have from 2 to 12 carbon atoms; and

- (iii) from 15 to 40% by weight of a third monomeric material which comprises one or more alpha, beta - ethylenically unsaturated carboxyl-containing monomers having from 3 to 15 carbon atoms, an anhydride thereof or a partial ester thereof in the case of a polycarboxylic monomer;

wherein the parts of A and C taken together total 100 parts by weight and the ratio of the monomeric materials renders the binding agent soluble in a dilute aqueous alkaline solution having a pH of 9 to 14 and wherein the binding agent is such that (i) the photopolymerizable composition is flexible without the need for an external plasticizer and (ii) it has a viscosity of at least 2,000 cps at 25°C, as determined by a Brookfield Viscometer, in 40% by weight solution in methyl ethyl ketone.

In brief, the advantages of the invention are obtained by selecting a preformed, compatible macromolecular binding agent which is a copolymer of (1) a styrene-type monomer, (2) an acrylate-type monomer, and (3) an unsaturated carboxyl-containing monomer. The first component lends hardness and chemical resistance to the polymer; the second, flexibility and plasticity to the polymer; and the third, alkali-solubility.

The photopolymerizable compositions of this invention comprise (1) from 10 to 60 parts by weight of one or more addition polymerizable non-gaseous ethylenically unsaturated compounds, (2) 40 to 90 parts by weight of the aforesaid binding agent, and (3) from 1 to 10 parts by weight, based upon 100 parts by weight of (1) and (2) of a conventional free-radical photoinitiator. Up to 5 parts by

weight of a conventional thermal addition polymerization inhibitor may also be added, preferably from 0.005 to 2.0 parts. Additionally, the compositions may contain suitable dyes and pigments and other additives, such as plasticizers and adhesion promoters, as may be necessary to enhance the physical and chemical properties of the photopolymerizable composition.

The ethylenically unsaturated compound must contain at least one terminal ethylenic group ($CH_2=C<$), must have a boiling point above 100°C. at atmospheric pressure and must be capable of forming a high polymer by free-radical photo-initiated, chain propagating addition polymerization. Such compounds are disclosed in U.S. Patent No. 2,760,863.

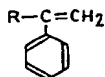
Preferably, the compounds are liquid or solid under ambient conditions, have 1 to 4 or more terminal ethylenic groups, preferably 2 or more, and a plasticizing action on the polymeric binder. Suitable compounds, which may be used alone or in admixture, include an alkylene or a polyalkylene glycol diacrylate prepared from the alkylene glycols having 2 to 15 carbons or the polyalkylene ether glycols of 1 to 10 ether linkages.

Because of their generally more rapid rate of insolubilization on exposure, presumably due to a relatively rapid establishment of a network polymer structure, an outstanding class of the low molecular weight addition polymerizable components are those having a plurality of addition polymerizable ethylenic linkages, particularly when present as terminal linkages, and especially those wherein at least one and preferably most of such linkages are conjugated with a double bonded carbon, including carbon double bonded to carbon and to such heteroatoms as nitrogen, oxygen, and sulfur. Outstanding are such materials wherein the ethylenically unsaturated groups, especially the vinylidene groups, are conjugated with ester or amide structures. The following specific compounds are further illustrative of this class: unsaturated esters of polyols, particularly such esters of the methylene carboxylic acids, e.g., ethylene glycol diacrylate; diethylene glycol diacrylate; tetraethylene glycol diacrylate; glycerol diacrylate; trimethylolpropane triacrylate; glycerol triacrylate; ethylene glycol dimethacrylate; 1,3 - propylene glycol dimethacrylate; 1,2,4 - butane triol trimethacrylate; 1,4 - benzene - diol dimethacrylate; pentaerythritol tetramethacrylate; 1,3 - propanediol diacrylate; 1,5 - pentanediol dimethacrylate; the bis - acrylates and bis - methacrylates of polyethylene glycols and ethoxylated alcohols and phenols, such as bis 4,4' - (2 - hydroxyethyl)phenyl - 2,2' - propane; unsaturated amides, particularly those of the methylene carboxylic acids, and especially those of alpha, omega - diamines and oxygen - interrupted omega - diamines, such as methylene bis -

acrylamide; methylene bis - methacrylamide; 1,6 - hexamethylene bis - acrylamide; diethylene triamine tris - methacrylamide; bis - (methacrylamidopropoxy)ethane; beta - methacrylamidoethyl methacrylate; N - [(beta - hydroxy - ethyloxy)ethyl] acrylamide; vinyl esters such as divinyl succinate, divinyl adipate, divinyl phthalate, divinyl terephthalate, divinyl benzene - 1,3 - disulfonate, and divinyl butane - 1,4 - disulfonate; and unsaturated aldehydes, such as sorbaldehyde (hexadienal). Mixtures of such compounds may also be used such as a mixture of trimethylolpropane triacrylate and tetraethylene glycol diacrylate or a mixture of bis - phenol A diacrylate and tetraethylene glycol diacrylate.

The preferred monomeric compounds are di- or poly - unsaturated, but mono - unsaturated monomers can also be used. The amount of monomer added varies with the particular binding agent.

The styrene-type constituent of the polymeric binding agent has the general formula:



wherein R is hydrogen or an alkyl group having from 1 to 6 carbon atoms or a halogen atom. The benzene ring may be ring substituted by nitro, alkoxy, acyl, carboxyl, sulfo or hydroxyl groups or halogen atoms. Whilst from 1 to 5 such substituents may be present, preferably, substitution is effected by a single alkyl group such as a methyl or t - butyl group. Most preferred of these compounds are styrene, alpha - methylstyrene, para - methylstyrene and para - t - butylstyrene. Mixtures of the styrene-type monomers may be used.

The acrylate-type component of the polymeric binding agent is an alkyl or hydroxy-

alkyl acrylate or methacrylate wherein the alkyl group has from 1 to 12, preferably from 1 to 6, carbon atoms and the hydroxyalkyl group has from 2 to 12 carbon atoms. Examples of these materials include methyl methacrylate, ethyl acrylate, hydroxypropyl methacrylate, hydroxyethyl methacrylate and hydroxyethyl acrylate. Also, advantageously, mixtures of two or more of the acrylate-type compounds may be used.

The third comonomer component is one or more alpha, beta - ethylenically unsaturated carboxyl-containing monomers having from 3 to 15 carbon atoms, preferably from 3 to 6. The preferred compounds are acrylic acid and methacrylic acid. Other acids which may be used are cinnamic acid, crotonic acid, sorbic acid, itaconic acid, propiolic acid, maleic acid, and fumaric acid, or the corresponding half esters or, where possible, the corresponding anhydride.

The ratio of the three monomeric components in the binder must be selected so that the resultant photopolymerizable composition incorporating such binder has the following properties: firstly, the photopolymerizable composition must be flexible and hard, but not tacky; secondly, the unexposed photopolymerizable material must be soluble in a dilute aqueous alkali solution having a pH of 9-14; thirdly, the photopolymerized material must be resistant to mildly alkaline plating solutions or etchants (such as copper pyrophosphate plating baths having a pH of about 8.5); fourthly, a 40% by weight methyl ethyl ketone solution of the binder should have a viscosity of at least 2,000 centipoise at 25°C, preferably from 2,500 centipoise to 8,000 centipoise, as measured by the Brookfield Viscometer.

The percentages by weight of the three types of monomeric material used in preparing the binder are set forth in the following table:

	Binder Component	Broad Range	Preferred Range
85	Styrene-type	40-60%	45-55%
	Acrylate-type	15-45%	25-35%
	Carboxylic acid-type	15-40%	18-30%

In forming dry films, the coating and drying method used in the laboratory is as follows. A coating solution is prepared by stirring all of the ingredients of the photopolymerizable composition in a methylethyl ketone solution. The solution is diluted by the addition of additional ketone to a viscosity of 100 to 200 centipoises and thereafter coated onto a 10 foot long, 5 inch wide polyester section stretched over a heat hardened glass sheet. A uniform thin coating is obtained by using a Meyer rod or a Gardner draw-down knife. The thickness is controlled so that a 1 to 2 mil thick film is obtained after drying.

Drying may be accomplished by, for

example, using a 150 watt, hot-air fan dryer. The dryer is located at one end of a lab-made tunnel covering the entire area to be dried. Hot air is forced through the tunnel continually for 20 minutes until all but a residual amount of solvent, approximately 0.1-2%, is evaporated from the film. This residual solvent does not interfere with the proper chemical and physical performance of the "dry" film resist.

The flexibility of the dried film is tested by crumpling the film into a loose ball and then smoothing the film out. The many sharp folds introduced into the film by this procedure will cause the film to crack or fall

apart if the film is too brittle. A good flexible film remains as a continuous sheet.

Flexibility and the degree of latitude during drying may be tested by overdrying a film sample in a forced air convection oven for 10 min. at 180°F. The overdried sample is then tested as described above.

There are no accepted industry standards for testing the cold flow properties of thin, 1—2 mil, unsupported photopolymer films which can be directly related to the tendency of the film to cold flow. The best method is to produce at least one 500 foot roll of a 2 mil photopolymerizable film, wind the sample around the core at the conventional tension, and let the film stand on its edge at room temperature for an extended period. A good film will be free from edge fusion for up to six months at 65°—75°F.

Two qualitative tests which closely correlate with the foregoing empirical test to determine cold flow are the Sward hardness and the "cold-flow-under-vacuum" tests. The Sward hardness number is determined by comparing the surface hardness of the film sample to that of glass which is used as the control. The Sward rocker is first calibrated to give a reading of 100 for the glass and thereafter a reading is taken of the test sample laminated onto the same glass sheet. It has been found that a good 1 mil aqueous-developable film should have a Sward hardness number of from 10 to 20 and a good 2 mil film a hardness in the range of 8 to 14.

In the "cold-flow-under-vacuum" test as a static load, the sample of film is laminated to copper and, with the polyester base still in place, a narrow wire (12—13 mils in diameter) is placed on top. The whole system is put under a reduced pressure of 3 in. of mercury for 5 minutes. After treatment, the polyester base is carefully removed and the indentation made by the wire as well as the "oozing out from the edges" of the film are photographed. Photographs from experimental films are compared with films having known acceptable cold flow properties.

As noted, the resist from the practice of this invention is resistant to the usual plating and etching solutions. Most surprising is its resistance to the copper pyrophosphate solution which is used in pattern plating and has an extremely high alkalinity. Other solutions which leave the resist unaffected include ferric chloride, ammonium persulfate and chromic-sulfuric acid solutions.

The photoinitiators used in the compositions are preferably those activatable by actinic light and thermally inactive at 185°C. or below. These include the substituted or unsubstituted polynuclear quinones, such as 9,10-anthraquinone; 1-chloroanthraquinone; 2-chloroanthraquinone; 2-methylanthraquinone; 2-ethylanthraquinone; 2-tert-butylanthraquinone; octamethylanthraquinone; 1,4-

naphthaquinone; 9,10-phenanthraquinone; 1,2-benzanthraquinone; 2,3-benzanthraquinone; 2-methyl-1,4-naphthaquinone; 2,3-dichloronaphthaquinone; 1,4-dimethylanthraquinone; 2,3-dimethylanthraquinone; 2-phenylanthraquinone; 2,3-diphenylanthraquinone; the sodium salt of anthraquinone alpha-sulfonic acid; 3-chloro-2-methylanthraquinone; retenequinone; 7,8,9,10-tetrahydronaphthacenequinone; and 1,2,3,4-tetrahydrobenz(a)anthracene-7,12-dione.

Also useful as photo-initiators are: vicinal ketalonyl compounds, such as diacetyl and benzil; alpha-ketalonyl alcohols and ethers, such as, benzoin, pivaloin; benzoin methyl and ethyl ethers, and alpha-hydrocarbon substituted aromatic acyls, e.g., alpha-methylbenzoin, alpha-allylbenzoin and alpha-phenylbenzoin; and alpha, alpha-dialkoxyacylphenones, e.g., alpha, alpha-diethoxyacetophenone. The preferred initiators are aromatic ketones, e.g., benzophenone and 4,4'-bis-dialkylamino-benzophenones particularly, the dimethylamino compound known as Michler's Ketone.

While it is generally desirable to include an inhibitor to prevent thermal polymerization during drying and storage, it is not absolutely essential to the photopolymerizable composition. Thermal polymerization inhibitors which may be in preferred compositions include p-methoxyphenol, hydroquinone, and alkyl and aryl-substituted hydroquinones and quinones, tert-butyl catechol, pyrogallol, copper resinate, naphthylamines, beta-naphthol, cuprous chloride, 2,6-di-tert-butyl p-cresol, 2,2-methylenebis-(4-ethyl-6-tert-butylphenol), phenothiazine, pyridine, nitrobenzene, dinitrobenzene, p-toluquinone, chloranil, aryl phosphites, and aryl alkyl phosphites.

If desired, the compositions may contain dyes and pigments. Suitable colorants will be compatible with the photosensitive compositions and not interfere appreciably with the photosensitivity of the composition. The following specific compounds are illustrative: Fuchsine (C.I. 42510); Auramine Base (C.I. 41000B); Calcocid Green S (C.I. 44090); Para Magenta (C.I. 42500); Tryparosan (C.I. 42505); New Magenta (C.I. 42520); Acid Violet RRH (C.I. 42425); Red Violet 5RS (C.I. 42690); Nile Blue 2B (C.I. 51185); New Methylene Blue GG (C.I. 51195); C.I. Basic Blue 20 (C.I. 42585); Iodine Green (C.I. 42556); Night Green B (C.I. 42115); C.I. Direct Yellow 9 (C.I. 19540); C.I. Acid Yellow 17 (C.I. 18965); C.I. Acid Yellow 29 (C.I. 18900); Tartrazine (C.I. 19140); Supramine Yellow G (C.I. 19300); Buffalo Black 10B (C.I. 27790); Naphthalene Black 12R (C.I. 20350); Fast Black L (C.I. 51215); Ethyl Violet (C.I. 42600); Pontacyl Wool Blue BL (C.I. 50315); Pontacyl Wool Blue GL (C.I.

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52320). (Numbers obtained from the second edition of The Color Index).

In use the photopolymerizable compositions mounted upon a substrate are exposed to a source of actinic radiation. This exposure may be through a half-tone image or a process transparency, e.g., a process negative or positive, a stencil, or a mask. The exposure may also be through a continuous tone, negative or positive image. The exposure may be by the contact or projection method, with or without a cover layer impervious to oxygen over the photopolymerizable layer or by projection using a cover layer. Thus at least one predetermined area of the photopolymerizable composition will be exposed. These procedures are well known to those skilled in the art. The substrate may be of copper or of a copper alloy.

Since free-radical generating addition-polymerization initiators activatable by actinic radiation generally exhibit their maximum sensitivity in the ultraviolet range, the radiation source should furnish an effective amount of this radiation. Both point or broad radiation sources are effective. Such sources include carbon arcs, mercury-vapor arcs, fluorescent lamps with ultraviolet radiation-emitting phosphors, argon glow lamps, electronic flash units and photographic flood lamps. Of these, the mercury-vapor arcs, particularly the sun lamps, are most suitable. In certain circumstances it may be advantageous to expose with visible light, using a photoinitiator sensitive in the visible region of the spectrum, e.g., 9,10-phenanthraquinone. In such cases, the radiation source should furnish an effective amount of visible radiation. Many of the radiation sources listed above furnish the required amount of visible light.

The photopolymerizable compositions after exposure may be developed in order to strip any unexposed portions of the photopolymerizable layer, e.g., by impingement of spray jets, with agitated immersion, brushing or scrubbing to give the desired images using aqueous bases, i.e., aqueous solutions of water-soluble bases in concentrations generally in the range from 0.01% to 10% by weight. After such development is completed the photopolymerizable layer is treated to permanently modify the developed portion of the substrate.

Suitable bases for the development include the alkali metal hydroxides, e.g., lithium, sodium, and potassium hydroxide; the base-reacting alkali metal salts of weak acids, e.g., lithium, sodium, and potassium carbonates and bicarbonates; amines having a base-ionization constant greater than about 1×10^{-6} , e.g., primary amines, such as benzyl, butyl and allyl amines; secondary amines, e.g., dimethylamine and benzyl methyl amine; tertiary amines, e.g., trimethylamine, and triethylamine; primary, secondary, and tertiary

hydroxyamines, e.g., propanol, diethanol and triethanol amines, and 2-amino-2-hydroxy-methyl-1,3-propanediol; cyclic amines, e.g., morpholine, piperidine, piperazine, and pyridine; polyamines, such as hydrazine, ethylene and hexamethylene diamines; the water-soluble basic salts, e.g., the carbonates and bicarbonates of the above amines; ammonium hydroxide and tetra-substituted ammonium hydroxides, e.g., tetramethyl-, tetraethyl-, trimethylbenzyl-, and trimethylphenylammonium hydroxides, sulfonium hydroxides, e.g., trimethyl-, diethylmethyl-, dimethylbenzylsulfonium hydroxides, and the basic soluble salts thereof, e.g., the carbonates, bicarbonates and sulfides; alkali metal phosphates and pyrophosphates, e.g., sodium and potassium triphosphates and sodium and potassium pyrophosphates; tetra-substituted (preferably wholly alkyl) phosphonium, arsonium, and stibonium hydroxide, e.g., tetramethylphosphonium hydroxide.

The photopolymerized compositions can generally be removed by immersion in heated aqueous solutions of strong alkalis or, if desired, in proprietary stripping materials well known in the art.

The following examples further illustrate the invention.

Example I

The following solutions were coated onto 1 mil thick polyester film, and dried in a current of hot air, provided by a GE-1500 watt fan drier, for 20 minutes. The dry thickness of the sensitized layers was about 1 mil. The dried layers were covered with a 1 mil thick polyethylene film. Solution A shows the practice of the invention while Solution B is a control solution.

Solution A

a) Copolymer of 50% by weight of styrene, 20% by weight of methyl methacrylate, 10% by weight of ethyl acrylate, and 20% by weight of methacrylic acid; viscosity of 40% by weight methyl-ethyl ketone solution = 4,500 cps at 25°C.	40.0 g	105
b) Ethoxylated Bisphenol-A diacrylate*	14.0 g	110
c) Tetraethylene glycol diacrylate	7.0 g	115
d) Benzophenone	2.25 g	
e) 4,4'-bis-(dimethylamino)-benzophenone	0.30 g	
f) Hydroquinone	0.03 g	120
g) Benzotriazole	0.12 g	
h) Dyes	0.07 g	
i) Methylene ketone	210.0 g	

*SR-349, Trademark of Sartomer Industries for the diethoxylated compound.

- Solution B
- 5 a) Copolymer of 75% by weight of styrene and 25% by weight of methacrylic acid, viscosity of 40% by weight solution in methylethyl ketone is 1,000 cps at 25°C 40.0 g
- b) Trimethylolpropane triacrylate 14.0 g
- c) Tetraethylene glycol diacrylate 7.0 g
- 10 d) Triethylene glycol diacetate 1.02 g
- e) Tricresyl phosphate 2.28 g
- f) Benzophenone 2.25 g
- g) 4,4' - bis - (dimethylamino)-benzophenone 0.30 g
- 15 h) 2,2' - methylene - bis - (4 - ethyl - 6 - tert - butylphenol) 0.30 g
- i) Benzotriazole 0.15 g
- j) Dyes 0.07 g
- k) Methyl ethyl ketone 210.0 g
- 20 A piece of copper-clad, epoxy fiberglass board was cleaned by scouring with an abrasive cleanser, swabbing and thoroughly rinsing in water. It was then given a 20 second dip in a 12% solution of hydrochloric acid, rinsed again with water and dried with air jets.
- 25 The polyethylene cover sheet was removed from a section of the sandwiched photopolymerizable element. The bared resist coating with its polyester support was laminated to the clean copper with the surface of the photopolymerizable layer in contact with the copper surface, using rubber covered rollers operating at a rate of 2 feet per minute at 250°F., with a pressure of 3 pounds per linear inch at the nip. The resulting sensitized copper-clad board, protected by the polyester film, was exposed to light through a high-contrast transparency for a period of 30 seconds using a 400 watt, 50 ampere mercury vapor lamp at a distance of 12 inches.
- 30 The polyester (polyethylene terephthalate) support film was peeled off and the exposed resist layer developed by agitating the board in a tray containing a 1%—1.5% by weight aqueous solution of potassium hydroxide together with a small amount of a surfactant for approximately 1 minute followed by a water rinse. This method of development is satisfactory for the composition of Solution A as well as of Solution B.
- 35 The surface of the exposed copper was further cleaned after development by dipping the board into a 20% by weight ammonium persulfate bath for 30 seconds, washing copiously with water, dipping for 30 seconds in a 20% by weight solution of hydrochloric acid in water, rinsing with water, then drying the board with jets of air. This cleaned board was then plated for 45 minutes at 30 amperes per square foot in a copper pyrophosphate plating bath at 55°C. Both resist compositions protected the underlying copper surface equally well from attack by components of the copper pyrophosphate plating bath.
- 40 The major difference between the two compositions is that Solution B employs a polymeric binder which in itself is a very poor, brittle film-former and external plasticizers (components (c) and (d) in Solution B) have to be included in the formulation to impart sufficient flexibility to the photosensitive resist film, while the copolymer described in Solution A is internally plasticized and is a much improved film-former. This copolymer significantly improves the drying latitude, integrity (film cohesion) and resistance to cold-flow or creep under static load of the photoresist product.
- 45 The flexibility of the films formed from the two solutions is tested by removing the polyethylene cover sheet from a strip of the sandwich structure, crumpling the supported film into a ball, and smoothing it out as described previously.
- 50 The flexibility test is also performed on films formed from Solutions A and B that have been dried in a forced air convection oven at 180°F. for 10 minutes, in addition to the normal drying procedure, to determine the drying latitude of the photopolymerizable resist film. Good drying latitude is an important requirement for a commercial dry film resist because such a product is not unduly dependent on residual solvent for flexibility and it has good shelf-life.
- 55 In the following Table, compositions from Solutions A and B are rated to indicate the significant differences between the two films regarding flexibility, surface tackiness, and drying latitude.

TABLE A

	Composition	Conventional Drying		After Extra Drying	
		Flexibility	Surface Tackiness	Flexibility	Surface Tackiness
105	Solution A	Good	Low	Good	Low
	Solution B	Fair	Slightly Tacky	Poor	Low

- 110 Cold-flow or plastic creep under a static load is a serious problem with dry film resists in general. Dry resists are sold as rolls of various lengths and widths. These rolls are wound under a certain amount of tension, to reduce "telescoping" or slipping of sub-

sequent layers past one another, which induces plastic creep. The effects of cold-flow are edge fusion or the fusing together of edges of contiguous layers, with the result that the roll cannot be unwound without removing some of the photopolymerizable layer from its polyester base, and the development of pinholes or even larger discontinuities within the dry film. Such a product is not acceptable to the customer because the resist will not polymerize during exposure in the areas where it has been separated from its base and pinholes can result in breaks within the printed circuit conductor lines.

Cold-flow is especially pronounced with aqueous processable dry film resists of the prior art, of which the composition in Solution B is a typical example, because the binder resin includes a large proportion (usually 20%—25%) of carboxylic acid-containing side chain segments. These segments tend to make the film brittle. The film is made flexible with external plasticizers which increase surface tackiness and contribute heavily to creep. The composition in Solution A is free from these shortcomings because the plasticizing components are an integral part of the binder polymer backbone.

Using the cold-flow test described above, the wound dry film rolls are stored and examined. Under these conditions, a 2 mil thick dry film photoresist made from the composition in Solution B showed significant signs of cold-flow within two weeks and the roll became unsalable after one month of storage. The film manufactured from the coating liquid described in Solution A, on the other hand, was free from edge fusion or internal pinholing even after seven months storage.

Using the Sward hardness test, the following results are obtained for the compositions of Solutions A and B:

TABLE B
Sward Hardness

Composition	1 mil film	2 mil film
Solution A	16—18	10—12
Solution B	8—10	4—6

Photographs of experimental films were compared with those from resist samples known to have acceptable cold-flow properties. The film from Solution A showed significantly less wire indentation than the corresponding film from Solution B, and very little "oozing out" at the edge.

Example II

The following composition was prepared, coated onto a 1 mil thick polyester film, dried to a thickness of approximately 1 mil as

described in Example I, and covered with polyethylene.

Solution C

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|---|---------|----|
| a) Copolymer of 50% by weight of styrene, 20% by weight of methyl methacrylate, 10% by weight of ethyl acrylate, and 20% by weight of methacrylic acid; viscosity of 40% methylethyl ketone solution is 4,500 cps at 25°C | 40.0 g | |
| b) Trimethylolpropane triacrylate | 13.33 g | 70 |
| c) Tetraethylene glycol diacrylate | 6.67 g | |
| d) Benzophenone | 2.25 g | |
| e) 4,4' - bis - (dimethylamino) - benzophenone | 0.30 g | 75 |
| f) 2,2' - methylene - bis - (4 - ethyl - 6 - tert - butylphenol) | 0.30 g | |
| g) Benzotriazole | 0.10 g | |
| h) Dyes | 0.07 g | |
| i) Methylethyl ketone | 210.0 g | |

A piece of copper-clad, epoxy fiberglass board was cleaned and laminated with the film made from the above composition. Another board was laminated with a control film prepared from the composition described in Solution B in Example I. Each board was exposed, developed, and plated in the copper pyrophosphate bath in accordance with the procedures outlined in Example I. Both resists gave excellent plating results in this hot, alkaline plating bath.

This example shows that the physical properties of the new dry film resist are affected by the monomeric components. Solution C contains trimethylolpropane triacrylate instead of ethoxylated Bisphenol-A diacrylate (Solution A). This change has no effect on the flexibility or drying latitude of the photopolymerizable resist film, but causes a reduction in its Sward hardness number, as shown in Table C.

TABLE C
Sward Hardness

Composition	1 mil film	2 mil film
Solution A	16—18	10—12
Solution C	12—14	8—10

Rolls made from the composition from Solution C were production coated to 2 mils and tested for cold-flow as described in Example I. The behaviour was better than that shown for the composition made from Solution B.

Example III

The following composition was prepared and coated onto a 1 mil thick polyester film, dried to the dry thickness of approximately 1 mil as described in Example I, and covered with polyethylene.

Solution D	
5	a) Copolymer of 40% by weight of styrene, 5% by weight of methyl methacrylate, 25% by weight of ethyl acrylate, and 30% by weight of meth- ketone solution is 5,800 cps acrylic acid; viscosity of 40% by weight methylethyl at 25°C
10	b) Trimethylolpropane triacrylate 40.0 g
	c) Tetraethylene glycol diacrylate 14.0 g
	d) Benzophenone 7.0 g
	e) 4,4' - bis (dimethylamino) - benzophenone 1.50 g
15	f) 2,2' - methylene - bis - (4 - ethyl - 6 - tert - butyl- phenol) 0.20 g
	g) Tolyltriazole 0.30 g
20	h) Benzotriazole 0.04 g
	i) Dye 0.12 g
	j) Methylethyl ketone 0.06 g
	k) 2 - methoxyethanol 210.0 g
	10.5 g

25 A piece of copper-clad, epoxy fiberglass board was cleaned and laminated with the above film, and the laminated board was exposed according to the procedure outlined in Example I. Unexposed portions of the film were washed off by agitating the board in a tray containing a 1.5% by weight solution of sodium carbonate in water for from 30 to 30 seconds.

35 The board was etched with a 45° Baumé solution of ferric chloride, rinsed and dried. The resist was removed from the copper by dipping for 2 minutes in a 3% solution of sodium hydroxide at 130°F. The result was a high quality printed circuit board.

40 The flexibility and drying latitude of the 1 mil photosensitive film was good and the Sward hardness number was 12-14.

Example IV

45 The photopolymerizable Solution A of Example I was coated onto zinc, magnesium, and copper printing plates. After drying in warm air to a dry thickness of about 1 mil, the photopolymerizable layer was coated with a dilute aqueous solution of polyvinyl alcohol and redried with warm air. The water-soluble polymer formed a thin protective barrier to oxygen. These pre-sensitized metal plates may be stored for extended periods.

50 Upon exposure to actinic light through a suitable photographic negative, the unexposed photosensitive layer and the water-soluble top-coat can be developed simultaneously, leaving the metal plate ready for etching. The photopolymerized image area then serves as an excellent resist for the deep-etching processes normally encountered in the fabrication of metal printing plates. These resists are resistant to the common etchants, e.g., ferric chloride and nitric acid, filming agents, and

banking agents commonly added to the etching mixture to control the geometry of the etch. 65

Example V

70 The procedure of Example IV is followed, except that a 1 mil thick film of polyester is used as a protective layer instead of a water-soluble polymer. Following exposure to actinic light, the protective layer is peeled off prior to developing in an aqueous alkaline solution. As in Example IV, the photopolymerized image area serves as an excellent resist for the deep-etching of printing plates. 75

Example VI

80 Solution A of Example I is coated onto a 1 mil thick polyester film, dried in air, and covered with a 1 mil thick polyethylene film. This three layer film sandwich can be stored in sheets or rolls in light-safe areas for indefinite periods of time. Prior to use, the polyethylene cover film is peeled off, and the photosensitive layer is placed in contact with a metallic plate of the type described in Example IV and backed by lamination. Upon exposure to actinic light, the protective polyester layer is peeled off and developed in aqueous alkaline solution. As in Example IV, the photopolymerized image area is an excellent resist for the deep-etching of printing plates. 85 90

Example VII

95 Solution A of Example I is coated onto thin aluminium plates as commonly used in offset lithography by procedures described in Example IV, V and VI. Following exposure to actinic light and development in aqueous alkaline solution, the photopolymerized image area serves as an excellent ink-receptor. It also has outstanding abrasion resistance. The resulting plates can be used with excellent results for offset lithographic printing. 100

Example VIII

105 Solution A of Example I is coated onto a woven, mesh-like substrate by procedures described in Examples IV, V, and VI. Following exposure to actinic light and development in aqueous alkaline solution, the photopolymerized image area serves as an excellent mask. This application has shown utility in silk-screen type printing. 110

WHAT WE CLAIM IS:—

1. A photopolymerizable composition comprising: 115

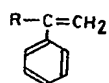
(A) from 10 to 60 parts by weight of one or more addition polymerizable non-gaseous compounds having a boiling point above 100°C., and at least one terminal ethylenic group 120

(B) from 1 to 10 parts by weight of a free-radical generating photoinitiator; and

(C) from 40 to 90 parts by weight of a

preformed macromolecular binding agent which is a polymer of

- (i) from 40—60% by weight of a first monomeric material which comprises one or more styrene-type compounds of the general formula:



wherein R is hydrogen, an alkyl group having from 1 to 6 carbon atoms or a halogen atom and the benzene ring may be substituted by from 1 to 5 substituents which are nitro, alkoxy, acyl, carboxyl, sulpho or hydroxyl groups or halogen atoms;

- (ii) from 15 to 45% by weight of a second monomeric material which comprises one or more alkyl acrylates, alkyl methacrylates, hydroxyalkyl acrylates or hydroxyalkyl methacrylates wherein the alkyl groups have from 1 to 12 carbon atoms and the hydroxyalkyl groups have from 2 to 12 carbon atoms; and
- (iii) from 15 to 40% by weight of a third monomeric material which comprises one or more alpha,beta - ethylenically unsaturated carboxyl-containing monomers having from 3 to 15 carbon atoms, an anhydride thereof or a partial ester thereof in the case of a polycarboxylic monomer;

wherein the parts of A and C taken together total 100 parts by weight and the ratio of the monomeric materials renders the binding agent soluble in a dilute aqueous alkaline solution having a pH of 9 to 14 and wherein the binding agent is such that (i) the photopolymerizable composition is flexible without the need for an external plasticizer and (ii) it has a viscosity of at least 2,000 cps at 25°C, as determined by a Brookfield Viscometer, in 40% by weight solution in methyl ethyl ketone.

2. A photopolymerizable composition as claimed in claim 1 wherein said first monomeric material is styrene.

3. A photopolymerizable composition according to either of claims 1 or 2 in which said second monomeric material is methyl methacrylate, ethyl acrylate, or a mixture thereof.

4. A photopolymerizable composition according to any of claims 1—3 in which said third monomeric material is methacrylic acid.

5. A photopolymerizable composition according to any of claims 1—4 in which said addition polymerizable material is one or more unsaturated esters of a polyol.

6. A photopolymerizable composition according to claim 5 in which the addition

polymerizable material is a mixture of trimethylolpropane triacrylate and tetraethylene-glycol diacrylate.

7. A photopolymerizable composition according to claim 5 in which the addition polymerizable material is a mixture of ethoxylated Bisphenol A diacrylate and tetraethylene - glycol diacrylate.

8. A photopolymerizable composition according to any of the preceding claims in which the photoinitiator is activatable by actinic light but thermally inactive at 185°C or below.

9. A photopolymerizable composition according to any of the preceding claims which also includes a thermal polymerization inhibitor.

10. A photopolymerizable composition according to any of the preceding claims in which said first monomeric material is present in a proportion of 45—55% by weight, said second monomeric material in a proportion of 25—35% by weight and said third monomeric material in a proportion of 18—30% by weight.

11. A photopolymerizable composition comprising:

(A) from 10 to 60 parts by weight of an addition polymerizable material consisting of one or more unsaturated esters of a polyol having a boiling point above 100°C and at least one terminal ethylenic group;

(B) from 1 to 10 parts by weight of a free-radical generating photoinitiator; and

(C) from 40 to 90 parts by weight of a preformed macromolecular binding agent which is a copolymer of 40—60% by weight of styrene, 15—45% by weight of methyl methacrylate and ethyl acrylate, and 15 to 40% by weight of methacrylic acid and wherein the parts of A and C taken together total 100 parts by weight and the ratio of the monomers renders the binding agent soluble in a dilute aqueous alkaline solution having a pH of 9 to 14 and wherein the binding agent is such that (i) the photopolymerizable composition is flexible without the need for an external plasticizer and (ii) it has a viscosity of at least 2,000 cps, at 25°C as determined by a Brookfield Viscosimeter, in 40% by weight solution in methyl ethyl ketone.

12. A laminate which comprises:

(A) a substrate of copper or a copper alloy;

(B) an intermediate photopolymerizable layer of a photopolymerizable composition according to any of claims 1—10; and

(C) a cover layer which is impervious to oxygen.

13. A process of making a photoresist which comprises:

(A) preparing a photopolymerizable layer of a photopolymerizable composition according to any of claims 1—10 on a substrate;

(B) exposing at least one predetermined

area of said photopolymerizable layer to actinic light; and

5 (C) developing said layer with a dilute aqueous alkaline solution so as to strip any unexposed portions of the photopolymerizable layer.

10 14. A process as claimed in claim 13 wherein the photopolymerizable layer, after said developing step is completed, is treated to permanently modify the developed portion of said substrate.

15 15. A photopolymerizable composition according to claim 1 and substantially as

hereinbefore described with reference to any one of Examples I—III.

16. A laminate according to claim 12 and substantially as hereinbefore described with reference to any of Examples IV—VI.

17. A process of making a photoresist according to claim 13 and substantially as hereinbefore described with reference to any of Examples IV—VIII.

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